Concentration measurements in silica and quartz nanofluids by optical fiber sensor

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ABSTRACT

The measurement of concentration in colloidal silica nanoparticles and quartz nanocrystals dispersions by using an optical fiber reflectometer is reported. The reflected light intensities assessed by the fiber sensor were applied on the computation of autocorrelation functions, and the decay rates were associated to the colloids concentrations. The sensor provided reliable results, with sensitivities of 0.45 wt% ms and 0.23 wt% ms on the analysis of quartz and silica dispersions, respectively, for concentrations <1wt%. The differences on decay rate profiles are probably due to the differences on particles morphology and average dimension, as observed in the scanning electron microscopy images.

Keywords: Nanofluids, optical fiber sensor, dynamic light scattering, silica, quartz.

1. INTRODUCTION

Nanofluids comprises stable colloids of nanoscaled materials dispersed in a base fluid. In particular, SiO_2-based suspensions present an attractive system for such technology, due to their physical and chemical properties, and ease of processing[1,2]. Current applications of colloidal silica includes quantum dots for biosensing[1], and general investigation and modeling in stability and concentration experiments[2]. Furthermore, studies also demonstrate the potential of application of quartz nanocrystals suspensions on the evaluation of redistribution processes, as well as phase-transition analysis[3].

Once the sample properties (thermal, mechanical, optical, or magnetic ones) depend on the characteristics of both dispersed and continuous phases, the nanofluids can be enhanced according to the composition, concentration and dimensions of nanoparticles[4]. In this sense, the assessment of particles concentration figures as a key factor in both production and application of the colloidal dispersions. Such measurement is usually performed by the dynamic light scattering (DLS) technique, in which the frequency variations due to particles scatterings are smaller than the frequency of incident light. These fluctuations are caused by translational and Brownian motions, yielding temporal variations in the detected light intensity[5,6]. Remarkably, optical fiber sensors have been successfully implemented for DLS measurements, allowing in-situ and minimally invasive analysis even in very concentrated dispersions[7].

Present paper reports the utilization of an optical fiber reflectometer on the measurement of SiO_2 nanofluids. The scattering data is processed by autocorrelation analysis, and the effect of colloids concentrations is investigated for both silica soot and quartz nanocrystals.

2. MATERIALS AND METHODS

2.1 Autocorrelation functions

According to DLS theory[6], the intensity autocorrelation function G_2 in time domain is given by the mean time average

$$G_2(\tau) = \langle I(t)\, I(t-\tau) \rangle, \quad (1)$$

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where $I(t)$ is the light intensity detected at time t, and τ is the correlation delay time. Function G_2 can be associated with the normalized field autocorrelation function g_1 according to the Siegert relation

$$G_2(\tau) = A + Bg_1^2(\tau) = A + B\exp(-2\Gamma\tau), \quad (2)$$

A and B are the baseline and coherence factor, respectively. Moreover, the decay rate $\Gamma = Dq^2$ can be expressed as a function of the particle translational diffusion coefficient D for spherical particles (Stokes-Einstein equation), and the magnitude of scattering vector q. The average particles properties in polydisperse samples can be estimated according to the average decay rate Γ_m, which is determined as a function of the unnormalized field autocorrelation function $G_1 = B^{1/2}g_1$,

$$\ln G_1(\tau) = \ln B^{1/2} - \Gamma_m\tau + K_2\tau^2/2 + K_3\tau^3/6 + \ldots, \quad (3)$$

where K_2, K_3, … are the moments of distribution of decay rates.

2.2 Optical fiber sensor

The schematic of the optical fiber Fresnel-based reflectometer[8] is shown in Figure 1. The light emitted by a 1310 nm continuous laser diode source is launched into a standard silica singlemode fiber. Part of the optical signal is derived using a coupler and then measured by a photodiode, serving as reference. The remaining light is delivered to the fiber end face (plane-polished with zirconia ferrule), which is directly immersed in the analyzed sample. The resulting light intensity, which comprises the contributions of particles scattering and reflection at the fiber-liquid interface[6], is subsequently derived by an additional coupler, being further detected by another photodiode. The measured data are acquired in 1 kHz sampling rate, and later post-processed by a routine developed under MATLAB environment.

2.3 Nanoparticles production

Silica nanoparticles were produced according to the flame aerosol method[9], by the oxidation and hydrolysis of $SiCl_4$ vapor in a H_2/O_2 flame. The raw halide material and the combustion and inert gases are delivered to 6 concentric nozzles silica torch, with the gases flow rates adjusted by mass flow controllers. The synthesized silica particles are axially deposited over a silica glass rod placed inside the reaction chamber, by controlling the target rotation and translation movements, as well as the temperature of deposition surface. Next, the soot is mechanically detached from the porous preform, and then grinded in a silica mortar in order to segregate the particles, producing a fine silica powder.

For obtaining the quartz nanocrystals, natural quartz sand was processed by high energy ball milling using silica media and balls. The raw material was previously cleaned and washed with water in order to remove the major impurities, and the grinding procedure was carried out at room temperature for 7 days under distilled water. Subsequently, the ground material was added to deionized and distilled water, and then subjected to decantation in a 1000 mL graduated cylinder for 48 hours. The transparent phase separated in the superior region of liquid column was collected using a pipette, and finally dried in a hot plate, yielding the nanoquartz powder.

2.4 Experimental procedure

Samples of silica and quartz nanofluids were prepared at room temperature in a two-step method[10], by dispersing the nanoparticles in distilled water. After mixing the solutions using a magnetic stirrer for 15 minutes, the samples were subjected to a supplementary ultrasound treatment for 1 hour in an ultrasonic bath, in order to enhance the stability of the SiO_2 colloids.

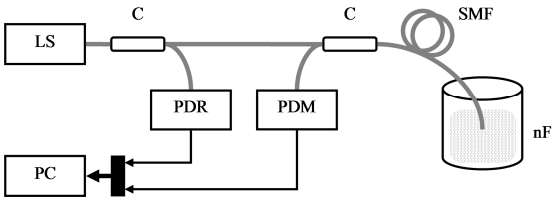

Figure 1. Schematic of the optical fiber reflectometer. LS: laser source; C: fiber coupler; SMF: singlemode fiber; PDR: reference photodetector; PDM: measurement photodetector; nF: nanofluid sample; PC: computer.

The effect of samples concentration on sensor response was assessed by measuring the reflected intensities at room temperature. The nanoparticles contents were varied with the increment of predetermined volumes of distilled water using a calibrated pipette, followed by 5 min mixing procedure using the stirrer. Each sample was analyzed for ~50 s, resulting in 50.000 data points per concentration. The I_R values are applied on the calculation of discrete intensity autocorrelation functions G_2, and consequently the unnormalized field autocorrelation functions G_1. Finally, the average decay rate for each sample is computed by fitting equation (3) as a function of the delay time τ, and the variations on decay rates are correlated to the nanoparticles concentration. In addition, the average particles sizes were estimated from the scanning electron microscopy (SEM) images (Figure 2) by using a MATLAB routine, by considering the Feret diameter in case of quartz nanocrystals.

3. RESULTS

The normalized field autocorrelation functions g_1 for representative samples are shown in Figure 3. It is worth noticing that all curves decay to ~0.101 for large delay time values ($\tau > 600$ ms), once the baselines of G_2 were set to 90% of their values in order to make $G_1 > 0$ during the calculations of logarithms. The average decay rates Γ_m were evaluated by fitting g_1 according to 9th degree polynomials ($R^2 \cong 0.995$), and the effect of concentration in Γ_m is presented in Figure 4. The decay rate increases with the particles content, as expected, due to the higher occurrence of multiple light scatterings, which affects the magnitude of scattering vector[6] q. Since the nanofluids were prepared from the same dispersed materials (silica soot or nanoquartz), the influence of particles diameter (and therefore the translational diffusion coefficient[6] D) can be assumed constant for all experiments. On the other hand, the quartz colloids produced higher Γ_m in comparison to the silica ones for the same concentration values. In addition to the differences on average diameters (134±3 nm and 99±2 nm for silica and quartz particles, respectively), which affects D, the silica particles morphology is practically homogeneous and spherical (Figure 2.a), whereas the quartz nanocrystals consist of a combination of irregular grains and needle-shaped structures (Figure 2.b). The light scattering for non-spherical particles is also dependent on the particles rotational diffusion coefficient[11], therefore the quartz nanofluids present an increase on decay rate in comparison to silica soot due to contribution of both particles size and morphology. Although such effect must be taken in account in case of estimating the particles dimensions, the concentration assessment regarding nanofluids preparation can be performed from a calibration curve, by assuming a previous knowledge concerning the characteristics of the silica soot or quartz nanocrystals. The fiber sensor sensitivities for low concentrations range (< 1 wt%) is 0.45 wt% ms and 0.23 wt% ms, for silica and quartz colloids, respectively.

4. CONCLUSION

The optical fiber reflectometer was successfully applied on the assessment of concentration in silica and quartz nanofluids. Although the sensor response is strongly affected by the nanoparticles morphology, the system can be utilized for practical concentration measurements if the colloid is formed from previously characterized materials. Further developments will focus on the application of the sensor on the monitoring of nanofluids preparation and separation procedures.

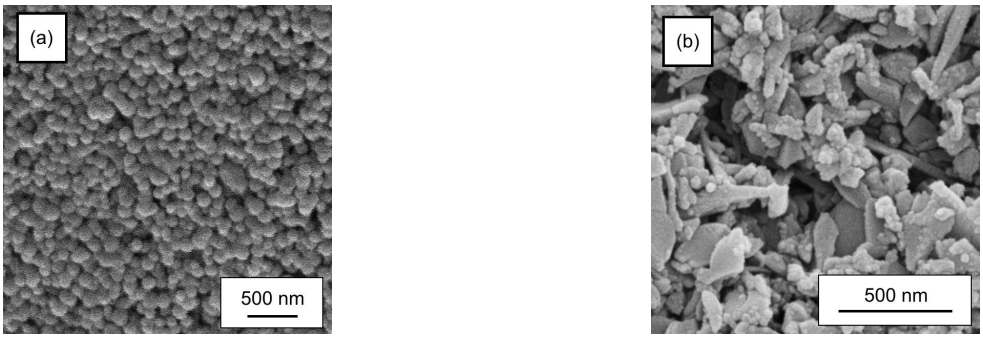

Figure 2. SEM images of produced a) silica and b) quartz nanoparticles. The samples were prepared by depositing droplets of concentrated nanofluids over aluminum specimen stubs, followed by drying in a hot plate for water evaporation. The silica soot was subsequently coated with a thin gold film using a Bal-Tec SCD 050 Sputter Coater, and analyzed in a Zeiss EVO MA 15 with LaB_6 thermionic cathode operating at 15 kV. The quartz nanocrystals were coated with amorphous carbon, and tested in a FEI Quanta 650 FEG with Schottky emission electron gun operating at 10 kV.

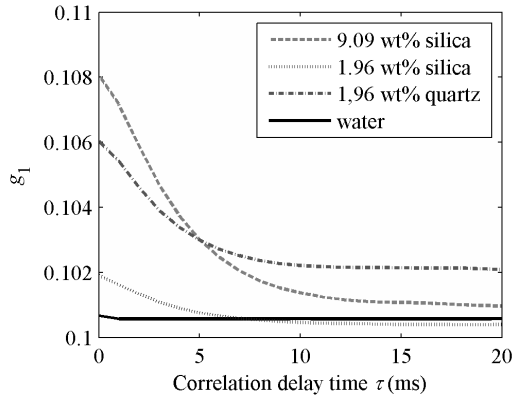

Figure 3. Field autocorrelation functions as function of delay time ($\tau \leq 20$ ms) for different samples. All curves decay to ~0.101 for $\tau > 600$ ms.

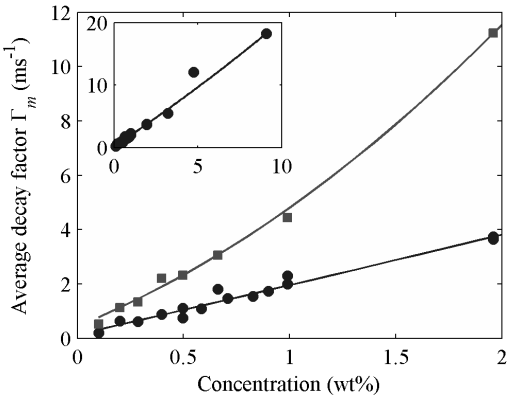

Figure 4. Effect of nanofluids concentration on average decay factor. Circles and squares correspond to silica and quartz dispersions, respectively. Inset: decay factor for silica nanofluids concentrations from 0.1 to 9.1 wt%. Data were fitted with $R^2 > 0.993$.

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